SCIENCE FOR CERAMIC PRODUCTION

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SPECIFICS OF SYNTHESIS OF CERAMICS WITH LOW CLTE

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The results of producing ceramic materials with low CLTE based on a cordierite-enstatite matrix are considered. Compositions promising for the production of heat-resistant ceramics with CLTE ranging from 0.058×10^{-6} to $-1.793 \times 10^{-6}\ K^{-1}$ are identified and recommended for application under abrupt thermal loads.

The rapid advancements in new high-temperature engineering involves the application of various construction materials capable of operating in state-of-the art plants (induction heaters, resistance furnaces, laser systems, plasma guns) under abrupt temperature differences without destruction and preserving their main operational parameters. Such materials should have mechanical strength and resistance to high temperatures and to be thermostable as well [1].

It is known that the thermal stability of material is an integral characteristic depending on many factors. The analysis of the criteria of thermal stability of ceramics indicates that this parameter depends mainly on such properties as the CLTE, mechanical strength, and elasticity modulus, which determine the main criterion of thermal resistance. A certain role is played by heat transfer conditions (temperature conductivity), size and shapes of articles. and other factors. The structure of the material is significant as well, since it determines the velocity of initiation and propagation of thermal cracks [2].

However, the prevalent factor determining the resistance of ceramics to thermal shocks is the CLTE; the lower this coefficient, the lower the probability of thermal stresses arising under in abrupt temperature changes. The CLTE of ceramics depend on its phase composition, the type and quantity of the cementing vitreous phase, and, to a certain extent, the texture and microstructure, which, in turn, depends on the degree and type of sintering [3 – 5].

Various research centers (Moscow Institute of Electroceramics, Kharkov Institute of Refractories, Belgorod Institute of Construction Materials, etc.) have carried out extensive research in the field of development of heat-resistant materials. Most frequently heat-resistant products are made of ceramic materials with low CLTE (below $2.0 \times 10^{-6}\ K^{-1}$) synthesized on the basis of cordierite, lithium-aluminosilicates, and aluminum titanate, which points to a limited number of little-expanding phases. However, these materials have substantial drawbacks: a narrow sintering interval (all specified materials), low density and mechanical strength (cordierite and tialite materials), insufficient refractoriness (lithium-bearing materials), or unstable CLTE (tialite) [1].

The analysis of literature and patent data indicates that a required set of properties ensuring high thermal resistance can be obtained by a rational combination of crystalline phases (little-expanding, high-strength, high-refractory) and by regulating the microstructure and texture of materials.

We have carried out extensive research in various oxide systems ($MgO – Al_2O_3 – SiO_2$, $Li_2O – MgO – Al_2O_3 – SiO_2$, $Al_2O_3 – SiO_2 – TiO_2$) and have obtained heat-resistant ceramics based on a combination of diverse crystalline phases [6 – 8]. The role of a little-expanding matrix was played by crystalline phases with low CLTE (cordierite, eucryptite, spodumene, tialite), and the strengthening phases were mullite, spinel, as well as additives of high-strength compounds (corundum, silicon carbide, etc.). A preset phase composition and a rational combination of crystalline phases in the considered systems have been achieved by designing initial compositions, using mineralizing additives, and modifying the conditions of synthesis.

The characteristics of materials developed on the basis of the specified systems are listed in Table 1. As can be seen, the rational combination of crystalline phases ensures a high heat resistance of materials with a wide range of other physicochemical parameters, which makes them suitable for service in diverse thermal cycling conditions. Thus, the main

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TABLE 1

System and additional components	Combination of crystalline phases	Main characteristics
$MgO – Al_2O_3 – SiO_2$ (electrocorundum, feldspars, phosphate binders, zircon, organic inclusions, BaO, ZnO, AlF_3, CaF_2, Na_2SiF_6)	Cordierite – mullite, cordierite – mullite – corundum, cordierite – spinel, spinel – cordierite – corundum	Refractoriness 1500 – 1670°C CLTE $(1.7 – 4.5) \times 10^{-6}$ K^{-1} Compressive strength 38 – 66 MPa Heat resistance 60 – 100 thermal cycles Water absorption 7 – 16% Apparent porosity 13 – 31% Volume resistivity $10^{12} – 10^{14}$ $\Omega \cdot cm$
$Li_2O – MgO – Al_2O_3 – SiO_2$ (ZnO, ZrO_2)	Eucryptite – cordierite, spodumene – cordierite, spodumene – spinel – cordierite, spodumene – spinel – enstatite	Refractoriness 1580°C CLTE $(0.4 – 1.4) \times 10^{-6}$ K^{-1} Compressive strength 27 – 60 MPa Heat resistance over 100 thermal cycles Water absorption 1.6 – 5.8% Apparent porosity 3.5 – 13.0% Volume resistivity $10^9 – 10^{10}$ $\Omega \cdot cm$
$Al_2O_3 – SiO_2 – TiO_2$ (MgO, CaO, SrO, BaO, ZrO_2, SnO_2, CeO_2, and titanium slag)	Mullite – tialite – rutile, mullite – rutile, mullite – corundum – rutile	Refractoriness 1650 – 1750°C CLTE $(1.1 – 5.6) \times 10^{-6}$ K^{-1} Compressive strength 20 – 66 MPa Heat resistance 40 – 100 thermal cycles Water absorption 0.1 – 6.6% Apparent porosity 0.3 – 18.0% Volume resistivity $10^{11} – 10^{12}$ $\Omega \cdot cm$ Acid resistance 99.4%

prerequisite for developing highly thermostable materials is ensuring a preset phase composition.

The experiments established that a promising method for raising the heat resistance of ceramics is modifying its structure by adding an additional crystalline phase whose CLTE differs from that of the matrix and which, accordingly, is capable of decreasing the volume and interphase stresses arising in thermal cycling. This has been proved using the combinations of a cordierite matrix with other presynthesized fillers (aluminosilicate and cordierite chamotte, corundum, silicon carbide, periclase-chromite, etc.) with different CLTE values (from 2.0 to 8.5×10^{-6} K^{-1}).

It is established that fillers should be introduced in the amount of 25 – 30% (here and elsewhere weight content, unless otherwise specified). In this case a slight increase in the CLTE of the total composite is observed, since the matrix of the material preserves its low values. A heterogeneous structure is formed in materials; chamotte-cordierite composites typically have a fragmentary structure, whereas corundum- and carborundum-cordierite composites have a near-skeleton structure. Under thermal loading, the first to break are the intergrain contacts between the cordierite matrix and the filler and the contacts between the phases as well. As a consequence, microcracks originated around the filler grains, which prevents the propagation of main destructive cracks. The microcrack structure is more intense in the case of using inert silicon carbide, which is characterized by the covalent chemical bond and the absence of a chemical reaction with the matrix.

Furthermore, silicon carbide plays the reinforcing role due to the presence of high-strength isometric needle-shaped crystals. If the CLTE of the filler differs from that of the matrix, the heat resistance of ceramics grows by 15 – 25%. The results of the experiments indicate that the granulometric composition of the matrix and the filler have great significance in the formation of a cracked structure. When the material in sintering partly consists of large particles (1 – 2 mm) separated by a fine fraction (below 0.1 mm), microcracks arise around the large particles due to difference in shrinkage. The fraction grain size has a certain impact on the elasticity modulus: the modulus decreases as the grain size increases (for instance for periclase-chromite filler from 125.6 to 103.1 MPa). This leads to a higher thermal resistance and, accordingly, the highest values of the elasticity modulus are registered in samples with carbide-silicon and aluminosilicate fillers with the grain size of 1 – 2 mm.

The type and layout of pores have a great effect on thermal stability as well. Materials with spheroid pores are the most resistant to mechanical and thermal stresses. To create such pores, it is recommended to introduce organic materials (up to 10 – 12%), whose burnout facilitates the formation of such pores. However, experiments have shown that burning out the components significantly raise the total porosity and decrease mechanical strength. In our opinion, an effective solution is introducing not more than 2 – 3% burning-out (particularly, hydrophobic) additives, and the optimum results are achieved when the hydrophobic additive is previously mixed with the finely dispersed component of the mixture. In this case open porosity decreases at the expense of the in-

creasing quantity of sealed pores. Burning-out additives can be lignin, coke, fuel oil, and other materials.

To decrease the CLTE to near-zero values and to improve thermomechanical properties, we have modified developed materials using additional components.

The contemporary production technology of little-expanding ceramics currently uses nontraditional materials produced by presintering, coprecipitation, or other methods which have a positive effect on lowering thermal expansion (Japan patent applications Nos. 52-29004 and 60-35312, U.S. patent No. 44795300, Germany patent application NOS 3616045) [9]. Such materials include compounds of different elements with phosphoric acid. Thus, ceramics based on $(ZnO)P_2O_7$, $Zr_2P_3O_{12}$, $Ba_{1x}Zn_4P_{6-2x}Si_{2x}O_{24}$, $2ZrO_2P_2O_5$, and $Ca_{0.5}Ti_2P_3O_{12}$ have negative CLTE values. Furthermore, adding 2 – 10% P_2O_5 to a cordierite matrix in which 10 mol.% MgO is replaced by ZnO and (or) Fe_2O_3 yields materials with CLTE up to -1.0×10^{-6} K^{-1}.

We selected phosphor-bearing zinc and zirconium compounds such as $Zn_3(PO_4)_2$ and $Zr_3(PO_4)_4$, as well as aluminum and manganese titanates to act as modifier crystalline phases. The initial ceramic matrix was the material synthesized in the cordierite-eucryptite system taken in the ratio of 60 : 40, whose CLTE is 0.95×10^{-6} K^{-1}.

Various mineralizing additives have been introduced in optimum composites: presintered tialite Al_2TiO_5, oxides and compounds ensuring the formation of phosphor-bearing phases in sintering of ceramics. Thus, the following additives were added to the initial ceramic matrix (%): 5.00 Al_2TiO_5 in mixture T1, 7.50 Al_2TiO_5 in mixture T2; 10.00 Al_2TiO_5 in mixture T3, 11.00 MnO_2 in mixture MT, 5.00 ZnO and 6.33 H_3PO_4 in mixture P, 12.70 ZrO_2 ands 5.36 H_3PO_4 in mixture ZP, and finally 12.70 ZrO_2 and 12.97 $(NH_4)_2HPO_4$ in mixture A.

Materials were fired at temperatures of 1100 and 1150°C. The CLTEs of synthesized materials are shown in Fig. 1 and the main physicotechnical properties of ceramics obtained under various firing temperatures are listed in Table 2.

It is established that the introduction of Al_2TiO_5 that has a high structure anisotropy decreases the CLTE which reaches negative values, up to -1.5×10^{-6} K^{-1} at the sintering temperature of 1150°C, furthermore increasing the quantity of tialite from 5 to 10% has no perceptible effect on the CLTE.

Tialite delays sintering, which increases the open porosity and water absorption in samples. However, considering the high melting point of Al_2TiO_5, it can be assumed that the service temperature of such material increases as well.

A composition of MnO_2 and TiO_2 has a favorable effect on the properties of the materials, since in addition to the fluxing effect, it significantly lowers the CLTE. Thus, at the firing temperature of 1100°C the CLTE is equal to -1.07×10^{-6} K^{-1} with good sinterability (water absorption approximately 2.0%).

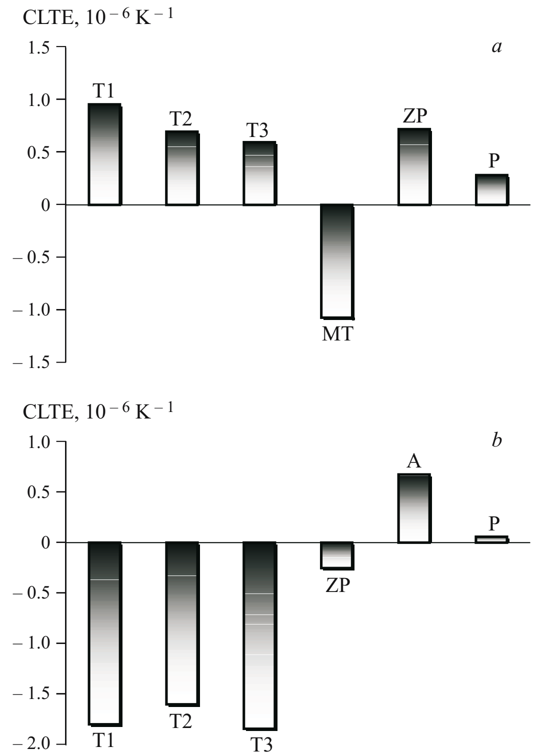

Fig. 1. CLTE of optimal ceramic compositions fired at 1100°C (*a*) and 1150°C (*b*).

Of special interest are the results of studying phosphor-bearing compounds of zinc and zirconium. It is established that sintering and formation of crystalline phases is more intense when phosphor oxide is introduced via phosphoric acid and not via monoammonium phosphate.

Furthermore, the sintering temperature is one of the most important factors affecting the thermal properties of ceramics considered. As the sintering temperature grows from 1100°C

TABLE 2

Composition	Water absorption, %	Porosity, %	Apparent density, kg/m^3
Firing temperature 1100°C			
T1	21.30	35.70	1676
T2	21.84	36.23	1659
T3	22.09	36.83	1670
MT	2.08	4.66	2238
P	20.45	34.96	1709
ZP	20.20	–	1737
A	11.10	28.60	1967
Firing temperature 1150°C			
T1	19.80	33.65	1700
T2	18.60	32.77	1761
T3	18.18	26.58	1462
MT	Was not determined		
P	13.23	17.94	1852
ZP	4.30	8.98	2087
A	11.10	28.60	1967

TABLE 3

Composition	Phase composition	CLTE, 10^{-6} K^{-1}
MT	$Li_2Mn_2O_4$, $Li_2Al_2Si_3O_{10}$, $MnAl_2O_4$, $LiAlSi_2O_6$, $MgSiO_3$	– 1.076
T1	Mg_2TiO_4, Al_2O_3, $Al_4Ti_2SiO_{12}$, $Li_2Al_2Si_3O_{10}$, $LiAlSi_2O_6$, $MgSiO_3$, $AlTiO_5$	– 1.793
ZP	$MgAl_2O_4$, $Li_6Si_2O_7$, $ZrLi_2P_2O_8$, $Mg_5Al_{2.4}Zr_{1.7}O_{12}$, $LiAlSi_3O_8$, $LiAlSi_2O_6$	– 0.252
P	$MgAl_2O_4$, $LiMgPO_4$, $ZnAl_2O_4$, $LiAlSi_3O_{10}$, $LiAlSi_2O_6$, $LiAlSi_3O_8$, $MgSiO_3$	0.058

to 1150°C, The CLTE of ceramics ZP changes from 0.75×10^{-6} to -0.25×10^{-6} K^{-1}, which is related to the quantitative distribution of crystalline components. The specified compositions with zinc- or zirconium-phosphor-containing phases were used to produce ceramics with CLTE close to zero (from 0.058×10^{-6} to -0.25×10^{-6} K^{-1}).

It is known [2, 3] that the main factor determining the thermomechanical properties of polycrystalline materials is their phase composition. The results of x-ray diffraction analysis of the optimum ceramic compositions are shown in Table 3.

It is established that the main crystalline phases of synthesized ceramics, regardless of the type of the modifying additive, are spodumene and spodumene-based solid solutions with different ratios of $Li_2O : Al_2O_3 : SiO_2$. Depending on the type of the modifier, additional compounds are formed in the ceramics, some of which had not been expected in calculating experimental compositions. Thus, the sample MT, apart from spodumene and enstatite, exhibits two manganese-bearing phases: galaxite (a type of spinel) and $Li_2Mn_2O_4$. Apparently, the combination of these phases is responsible for the negative values of the CLTE. It should be noted that the sintering temperature in manganese-bearing ceramics is 50 – 80°C lower than in other compositions, which leads to its impermeability due to the formation of low-melting eutectics.

Phosphor-bearing compositions, apart from the main phases of the initial ceramic matrix, contain complex compounds, mostly lithium-bearing zinc and zirconium phosphates. It is notable that the synthesized materials do not contain cordierite, although other magnesium-bearing phases are present. Probably, in the presence of lithium oxide and modifiers introduced the formation of cordierite becomes thermodynamically disadvantageous.

Technological recommendation have been prepared for producing heat-resistant ceramic materials based on the cordierite-eucryptite matrix with various mineralizing additives, which determine the formation of crystalline phases whose combinations ensure low CLTE values. As a consequence, heat resistant ceramics has been developed having the CLTE from 0.058×10^{-6} to -1.793×10^{-6} K^{-1}, heat resistance over 100 thermal cycles (800°C – water), a sufficient degree of sintering, and good mechanical properties.

The ceramic materials obtained can be used in areas of industry and engineering that require heat-resistant parts operating under abrupt thermal loads.

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